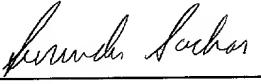


FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>217552US0PCT</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>09/926779</b>
INTERNATIONAL APPLICATION NO. <b>PCT/JP00/03910</b>	INTERNATIONAL FILING DATE <b>15 June 2000</b>	PRIORITY DATE CLAIMED <b>18 June 1999 (earliest)</b>		
TITLE OF INVENTION <b>NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY</b>				
APPLICANT(S) FOR DO/EO/US <b>KOTATO Minoru et al.</b>				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li><input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))             <ol style="list-style-type: none"> <li><input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li><input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> is attached hereto.</li> <li><input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))             <ol style="list-style-type: none"> <li><input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li><input type="checkbox"/> have been communicated by the International Bureau.</li> <li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li><input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li><input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li><input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li><input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>				
<p><b>Items 13 to 20 below concern document(s) or information included:</b></p> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li><input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li><input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li><input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li><input checked="" type="checkbox"/> Other items or information:</li> </ol>				
<p><b>Request for Priority/Drawings (3 sheets)</b></p> <p><b>Form PTO-1449</b></p>				

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>097926779</b>	INTERNATIONAL APPLICATION NO. PCT/JP00/03910	ATTORNEY'S DOCKET NUMBER <b>217552US0PCT</b>		
24. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>		
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>				
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b>				
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$890.00</b>		
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 <b>\$130.00</b>		
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	- 20 =	0	x \$18.00	<b>\$0.00</b>
Independent claims	- 3 =	0	x \$84.00	<b>\$0.00</b>
Multiple Dependent Claims (check if applicable).		<input type="checkbox"/>		<b>\$0.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$1,020.00</b>		
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.		<b>\$0.00</b>		
<b>SUBTOTAL =</b>		<b>\$1,020.00</b>		
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30      +	<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>		<b>\$1,020.00</b>		
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/>	<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>		<b>\$1,020.00</b>		
		<b>Amount to be: refunded</b>	\$	
		<b>charged</b>	\$	
a. <input checked="" type="checkbox"/> A check in the amount of <b>\$1,020.00</b> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No <b>15-0030</b> A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.				
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.				
SEND ALL CORRESPONDENCE TO:				
<b>Surinder Sachar</b> <b>Registration No. 34,423</b>  <b>22850</b>		 <b>SIGNATURE</b> <b>Norman F. Oblon</b> <b>NAME</b> <b>24,618</b> <b>REGISTRATION NUMBER</b> <b>Dec. 18 2001</b> <b>DATE</b>		

Rec'd PCT/PTO 28 MAY 2002

#5

217552US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF : :

MINORU KOTATO ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: 09/926,779 : :

FILED: DECEMBER 18, 2001 : :

FOR: NON-AQUEOUS ELECTROLYTE  
SECONDARY BATTERY

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

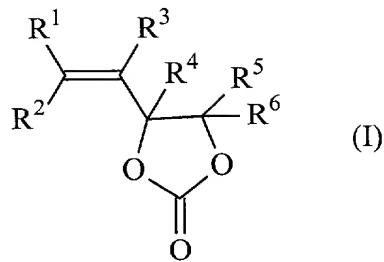
SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

1. (Amended) A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, wherein said non-aqueous solvent comprises a vinylethylene carbonate compound represented by the following formula (I) in an amount of from 0.01% to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein said negative electrode comprises a carbon-based material capable of absorbing and releasing lithium.

4. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein said non-aqueous solvent is a mixed solvent comprising a cyclic carbonate selected from the group consisting of alkylene carbonates having an alkylene group moiety of from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonates having an alkyl group moiety of from 1 to 4 carbon atoms, wherein the vinylethylene carbonate compound of formula (I) is present in an amount of not less than 20 vol-%, and wherein said cyclic and chain carbonates are present in an amount of not less than 70 vol-% based on the total solvent amount.

5. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the formula (I) comprises one or more solvents having a relative dielectric constant of not less than 25 and a flash point of not lower than 70°C.

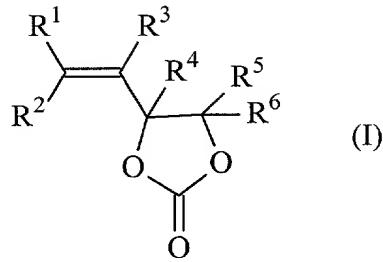
6. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the formula (I) has a relative dielectric constant of not less than 25.

7. (Amended) The non-aqueous electrolyte secondary battery according to Claim 5, wherein said solvent having a relative dielectric constant of not less than 25 is selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone.

8. (Amended) The non-aqueous electrolyte secondary battery according to Claim 5, wherein said solvent having a relative dielectric constant of not less than 25 is a mixture of ethylene carbonate and  $\gamma$ -butyrolactone.

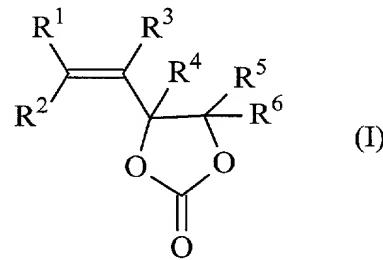
9. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein the lithium salt is at least one salt selected from the group consisting of LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>.

10. (Amended) A non-aqueous electrolyte for a non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium, said non-aqueous electrolyte comprising a solute and a non-aqueous solvent, wherein said non-aqueous solvent comprises a vinylethylene carbonate compound represented by formula (I) in an amount of from 0.01 to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

11. (Amended) A non-aqueous electrolyte for a non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium, said non-aqueous electrolyte comprising a solute and a non-aqueous solvent, wherein said non-aqueous solvent comprises one or more solvents wherein said one or more solvents have a relative dielectric constant of not less than 25, is present in an amount of not less than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by formula (I):



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

Please add the following new claims.

12. (New) The non-aqueous electrolyte secondary battery according to Claim 6,  
wherein said solvent having a relative dielectric constant of not less than 25 is selected from  
the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate,  
 $\gamma$ -butyrolactone and  $\gamma$ -valerolactone.

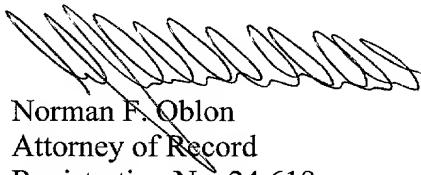
13. (New) The non-aqueous electrolyte secondary battery according to Claim 6,  
wherein said solvent having a relative dielectric constant of not less than 25 is a mixture of  
ethylene carbonate and  $\gamma$ -butyrolactone.

REMARKS

Claims 1-13 are active in the present application. Claims 1-11 have been amended to remove multiple dependencies and for clarity. Claims 12 and 13 are new claims. Support for the new claims is found in the original claims. No new matter is believed to have been added by this amendment. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

Stefan U. Koschmieder, Ph.D.  
Registration No. 50,238



**22850**

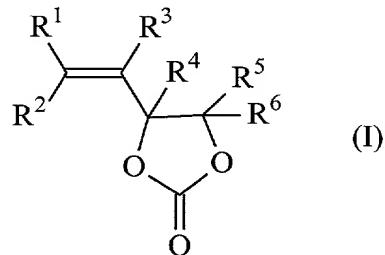
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Marked-Up Copy  
Serial No: 09/926,779  
Amendment Filed on:  
5-28-2002

IN THE CLAIMS

--1. (Amended) A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, [characterized in that] wherein said non-aqueous solvent [contains] comprises a vinylethylene carbonate compound represented by the following [general] formula (I) in an amount of from 0.01% to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. (Amended) The non-aqueous electrolyte secondary battery according to Claim 1, wherein said negative electrode [contains] comprises a carbon-based material capable of absorbing and releasing lithium.

4. (Amended) The non-aqueous electrolyte secondary battery according to [any one of Claims 1 to 3] Claim 1, wherein said non-aqueous solvent is a mixed solvent [containing] comprising a cyclic carbonate selected from the group consisting of alkylene carbonates [the] having an alkylene group moiety of [which each have] from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonates [carbonate the] having an alkyl group moiety of [which each have] from 1 to 4 carbon atoms, wherein [except] the vinylethylene carbonate compound of [the general] formula (I) [each] is present in an amount of not [smaller] less than 20 vol-%, [with the proviso that the content of] and wherein said cyclic and chain carbonates [accounts for not smaller] are present in an amount of not less than 70 vol-% based on the total solvent amount [thereof].

5. (Amended) The non-aqueous electrolyte secondary battery according to [any one of Claims 1 to 3] Claim 1, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the [general] formula (I) [contains] comprises one or more solvents [selected from solvents] having a relative dielectric constant of not [smaller] less than 25 and [exhibits] a flash point of not lower than 70°C.

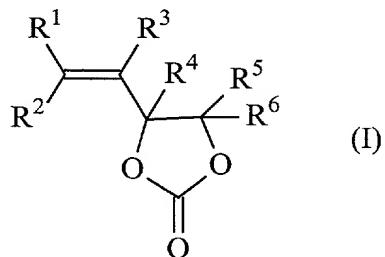
6. (Amended) The non-aqueous electrolyte secondary battery according to [any one of Claims 1 to 3] Claim 1, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the [general] formula (I) [is selected from solvents having] has a relative dielectric constant of not [smaller] less than 25.

7. (Amended) The non-aqueous electrolyte secondary battery according to Claim 5 [or 6], wherein said solvent having a relative dielectric constant of not [smaller] less than 25 is selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone.

8. (Amended) The non-aqueous electrolyte secondary battery according to Claim 5 [or 6], wherein said solvent having a relative dielectric constant of not [smaller] less than 25 is a mixture of ethylene carbonate and  $\gamma$ -butyrolactone.

9. (Amended) The non-aqueous electrolyte secondary battery according to [any one of Claims 1 to 8] Claim 1, wherein [said] the lithium salt is at least one salt selected from the group consisting of LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>.

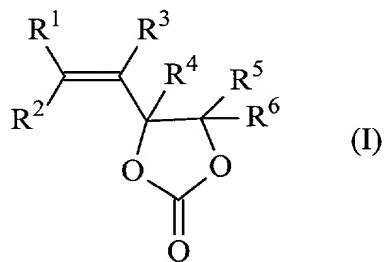
10. (Amended) A non-aqueous electrolyte for a non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium [which comprises], said non-aqueous electrolyte comprising a solute and a non-aqueous solvent, [characterized in that] wherein said non-aqueous solvent [contains] comprises a vinylethylene carbonate compound represented by [the following [general]] formula (I) in an amount of from 0.01 to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

11. (Amended) A non-aqueous electrolyte for a non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium [which comprises], said non-aqueous electrolyte comprising a solute and a non-aqueous solvent, [characterized in that] wherein said non-aqueous solvent

[contains] comprises one or more solvents [selected from solvents having] wherein said one or more solvents have a relative dielectric constant of not [smaller] less than 25,is present in an amount of not [smaller] less than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by [the following general] formula (I) [incorporated therein]:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

Claims 12-13 (New).--

3/PARTS

09/926779  
JC07 Rec'd PCT/PTO 18 DEC 2001

## Description

NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

## Technical Field

The present invention relates to a non-aqueous electrolyte secondary battery. More particularly, the present invention relates to a non-aqueous electrolyte secondary battery comprising an electrolyte containing a specific vinylidene carbonate compound. The battery of the invention is subject to minimized decomposition of electrolyte and exhibits a high capacity as well as excellent storage properties and cycle life performance at high temperatures.

## Background of the Invention

With the recent trend for the reduction of weight and size of electrical appliances, there has been a growing demand for lithium secondary battery having a high energy density. Further, with the expansion of the field to which the lithium secondary battery can be applied, it has been desired to further improve the battery performance.

Extensive studies have been heretofore made of secondary battery comprising metallic lithium as a negative electrode as battery which can attain a high capacity. However, the greatest technical problem that prevents the practical use of such a secondary battery was that when charge and discharge are repeated, metallic lithium grows in the form of dendrite and eventually reaches the positive electrode, causing

shortcircuiting in the battery.

To cope with this problem, a non-aqueous electrolyte secondary battery comprising as a negative electrode a carbon-based material capable of absorbing/releasing lithium such as artificial graphite and natural graphite has been proposed. In such a non-aqueous electrolyte secondary battery, lithium doesn't exist in metallic state, making it possible to inhibit the formation of dendrite and improve the battery life and safety. In particular, a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material such as artificial graphite and natural graphite has been noted as one meeting the demand for higher capacity.

However, in a non-aqueous electrolyte secondary battery comprising as a negative electrode any graphite-based electrode material, singly or in admixture with other negative electrode materials capable of absorbing and releasing lithium, if an electrolyte comprising as a solvent a propylene carbonate which normally is preferably used in a lithium primary battery is used, the decomposition reaction of the solvent proceeds violently on the surface of the graphite electrode, disabling the smooth absorption of lithium into the graphite electrode and smooth release of lithium from the graphite electrode.

On the other hand, ethylene carbonate undergoes little such decomposition and thus has been widely used as a main solvent of electrolyte for non-aqueous electrolyte secondary battery.

However, even if ethylene carbonate is used as a main solvent, the electrolyte decomposes on the surface of the electrode during charge and discharge, raising problems of drop of charge and discharge efficiency, deterioration of cycle performance, etc.

Further, ethylene carbonate exhibits a solidifying point as high as 36.4°C as compared with propylene carbonate and thus is not used singly but is used normally in admixture with a low viscosity solvent. For this reason, the electrolyte for lithium secondary battery comprising a graphite-based negative electrode normally comprises a mixture of ethylene carbonate and diethyl carbonate. However, since most such low viscosity solvents normally have a low boiling point, it is disadvantageous in that when added in a large amount, the solvent exhibits a lowered flash point, though giving good electrolyte properties. On the contrary, when added only in a small amount, it is disadvantageous in electrical conductivity and viscosity at low temperatures.

Under these circumstances, Japanese Patent Laid-Open No. 1992-87156 proposes an electrolyte comprising as a solvent a mixture of a specific compound which makes unsaturated carbon-carbon bond difficultly reactive with lithium chain-like, e.g., vinylethylene carbonate and 1,2-dimethoxyethane as a low boiling solvent in the same volume as that of the specific compound in a non-aqueous electrolyte battery comprising metallic lithium as a negative electrode.

On the other hand,  $\gamma$ -butyrolactone, etc., which is a cyclic ester, has a high relative dielectric constant as well as a low solidifying point and thus can be used without being mixed with a low viscosity solvent. However, the  $\gamma$ -butyrolactone-based electrolyte, too, is subject to progress of decomposition of  $\gamma$ -butyrolactone on the surface of the graphite electrode during charge, causing deterioration of battery performance.

Japanese Patent Laid-Open No. 1999-31525 proposes an electrolyte solvent comprising as a main component  $\gamma$ -butyrolactone and as a subsidiary component ethylene carbonate in an amount of from 15 to 35% by volume and practically comprising diethyl carbonate in an amount of not smaller than 16% by volume to inhibit the decomposition of  $\gamma$ -butyrolactone in a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material as a negative electrode.

However, the electrolyte disclosed in the above cited patent leaves something to be desired, though showing an excellent effect in its own way.

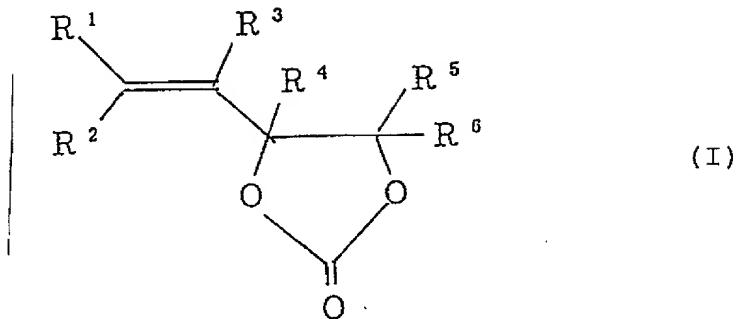
The present invention has been worked out to solve these problems. An object of the present invention is to provide a non-aqueous electrolyte secondary battery having a high energy density comprising a negative electrode containing a carbon-based material which is subject to minimized decomposition of electrolyte to exhibit a high charge and

discharge efficiency and show excellent storage properties and cycle life performance even at high temperatures.

#### Disclosure of the Invention

Under these circumstances, the inventors made extensive studies. As a result, it was found that the use of an electrolyte containing a specific vinyl ethylene carbonate compound as an electrolyte for non-aqueous electrolyte secondary battery comprising a negative electrode comprising a carbon-based material allows the efficient production of a stable lithium ion-permeable film on the surface of the negative electrode from the beginning of initial charge, making it possible to inhibit excessive decomposition of the electrolyte and hence improve the charge and discharge efficiency, storage properties and cycle life performance. The present invention has thus been worked out.

In other words, the essence of the invention lies in a non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, characterized in that the non-aqueous solvent contains a vinyl ethylene carbonate compound represented by the following general formula (I) in an amount of from 0.01% to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or C<sub>1</sub>-C<sub>4</sub> alkyl group.

The present invention also lies in a non-aqueous electrolyte for non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium which comprises a solute and a non-aqueous solvent, characterized in that the non-aqueous solvent contains a vinylethylene carbonate compound represented by the foregoing general formula (I) in an amount of from 0.01 to 20% by weight.

The present invention further lies in a non-aqueous electrolyte for non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium which comprises a solute and a non-aqueous solvent, characterized in that the non-aqueous solvent contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash

point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the following general formula (I) incorporated therein.

In the invention, the negative electrode preferably contains a carbon-based material capable of absorbing and releasing lithium, and the carbon-based material capable of absorbing and releasing lithium preferably comprises a carbon-based material having a d value of from 0.335 to 0.34 nm on lattice plane (002 plane) as determined by X-ray diffractometry.

In the non-aqueous electrolyte secondary battery of the invention, the non-aqueous solvent preferably is a mixed solvent containing a cyclic carbonate selected from the group consisting of alkylene carbonates the alkylene group moiety of which each have from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonate the alkyl group moiety of which each have from 1 to 4 carbon atoms except the vinylethylene carbonate compound of the general formula (I) each in an amount of not smaller than 20 vol-%, with the proviso that the content of said carbonates accounts for not smaller than 70 vol-% based on the total amount thereof, and the non-aqueous solvent except the vinylethylene carbonate compound of the general formula (I) preferably contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 and exhibits a flash

point of not lower than 70°C.

Further, the non-aqueous solvent except the vinylethylene carbonate compound of the general formula (I) preferably is selected from solvents having a relative dielectric constant of not smaller than 25. The solvent having a relative dielectric constant of not smaller than 25 is preferably ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone or  $\gamma$ -valerolactone, particularly a mixture of ethylene carbonate and  $\gamma$ -butyrolactone.

The lithium salt is preferably at least one salt selected from LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>) (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>.

#### Brief Description of the Drawings

Fig. 1 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Example 1 of the invention.

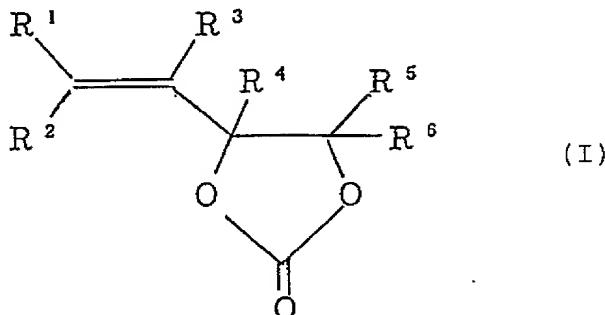
Fig. 2 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Comparative Example 1 of the invention.

Fig. 3 is a graph illustrating the capacity-potential curve developed by charge and discharge at the 1st cycle in Comparative Example 2 of the invention.

#### Best Mode for Carrying Out the Invention

The non-aqueous electrolyte secondary battery of the invention is characterized in that the non-aqueous solvent used

therein contains a vinylethylene carbonate represented by the following general formula (I):



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or C<sub>1</sub>-C<sub>4</sub> alkyl group.

In the general formula (I), when R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each are a C<sub>1</sub>-C<sub>4</sub> alkyl group, specific examples of the C<sub>1</sub>-C<sub>4</sub> alkyl group include methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, i-butyl group, and tert-butyl group. Preferred among these alkyl groups are methyl group and ethyl group. Specific examples of the vinylethylene carbonate compound represented by the general formula (I) include 4-ethenyl-1,3-dioxolane-2-one (occasionally referred to as "vinylethylene carbonate"), 4-ethenyl-4-methyl-1,3-dioxolane-2-one, 4-ethenyl-4-ethyl-1,3-dioxolane-2-one, 4-ethenyl-4-n-propyl-1,3-dioxolane-2-one, 4-ethenyl-5-methyl-1,3-dioxolane-2-one, 4-ethenyl-5-ethyl-1,3-dioxolane-2-one, 4-ethenyl-5-n-propyl-1,3-dioxolane-2-one, etc.

Among these vinylethylene carbonate compounds,

4-ethenyl-4-methyl-1,3-dioxolane-2-one is preferred, and vinylethylene carbonate is particularly preferred.

The compound of the general formula (I) may have substituents so far as the desired effect of the invention cannot be excessively impaired.

The content of the compound of the general formula (I) in the non-aqueous solvent is normally from 0.01 to 20% by weight, preferably from 0.01 to 10% by weight, more preferably from 0.1 to 10% by weight, even more preferably from 0.1 to 7% by weight, particularly from 0.1 to 5% by weight. When the content of the compound of the general formula (I) falls below 0.01% by weight, the protective film cannot be sufficiently effected. On the contrary, when the content of the compound of the general formula (I) exceeds 20% by weight, the electrolyte has a high viscosity and hence a low electrical conductivity, deteriorating the performance of the battery.

Examples of the non-aqueous solvent other than the compound of the general formula (I) to be used in the invention include cyclic carbonates such as ethylene carbonate, propylene carbonate and butylene carbonate, chain carbonates such as dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate, cyclic esters such as  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone, chain ethers such as tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran, chain ethers such as dimethoxyethane and dimethoxymethane, sulfur-containing

organic solvents such as sulfolane and diethylsulfolane, etc.

Two or more of these solvents may be used in admixture.

The non-aqueous solvent is a mixed solvent containing a cyclic carbonate selected from the group consisting of alkylene carbonates the alkylene group moiety of which each have from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonate the alkyl group moiety of which each have from 1 to 4 carbon atoms except the vinylethylene carbonate compound of the general formula (I) each in an amount of not smaller than 20 vol-%, with the proviso that the content of the carbonates accounts for not smaller than 70 vol-% based on the total amount thereof.

The term "vol-%" as used herein is meant to indicate one measured at room temperature, i.e., 25°C. However, any solvent which stays solid at 25°C shall be heated to its melting point where it is then measured in molten state.

Specific examples of the alkylene carbonate the alkylene group moiety of which has from 2 to 4 carbon atoms include ethylene carbonate, propylene carbonate, butylene carbonate, etc. Preferred among these alkylene carbonates are ethylene carbonate and propylene carbonate.

Specific examples of the dialkyl carbonate the alkyl group moiety of which has from 1 to 4 carbon atoms include dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate, ethylmethyl carbonate, methyl-n-propyl carbonate,

ethyl-n-propyl carbonate, etc. Preferred among these dialkyl carbonates are dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate. The mixed non-aqueous solvent may contain solvents other than carbonate.

Another preferred embodiment of the non-aqueous electrolyte secondary battery of the invention lies in a non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and a non-aqueous electrolyte made of a solute and a non-aqueous solvent, characterized in that the non-aqueous solvent contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the foregoing general formula (I) incorporated therein.

The non-aqueous solvent having a relative dielectric constant of not smaller than 25 to be used in the foregoing embodiment of the invention is not specifically limited. However, ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone, sulfolane, 3-methylsulfolane, dimethyl sulfoxide, etc. can be exemplified. Preferred among these non-aqueous solvents are ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone, and  $\gamma$ -valerolactone. A mixture of ethylene

carbonate and  $\gamma$ -butyrolactone is particularly preferred. Two or more of these solvents may be used in admixture. The combination of these solvents is not specifically limited.

Further, in the foregoing embodiment of the invention, to the non-aqueous solvent having a relative dielectric constant of not smaller than 25 may be added one or more non-aqueous solvents other than mentioned above, e.g., dialkyl (preferably having from 1 to 4 carbon atoms) carbonate such as dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate and ethylmethyl carbonate, cyclic ether such as tetrahydrofuran and 2-methyltetrahydrofuran, chain ether such as dimethoxyethane and dimethylmethane, chain ester such as methyl acetate and ethyl propionate. In this case, these solvents may be added in such a combination that the flash point of the non-aqueous solvents, including those added, is not lower than 70°C.

As the solute of the electrolyte to be used in the invention there may be used a lithium salt. The lithium salt is not specifically limited so far as it can be used as a solute. A specific example of such a lithium salt is an inorganic lithium salt selected from LiClO<sub>4</sub>, LiPF<sub>6</sub> and LiBF<sub>4</sub> or fluorine-containing organic lithium salt such as LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>) (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>. Preferred among these lithium salts are LiPF<sub>6</sub> and LiBF<sub>4</sub>. Two or more of these solutes may be used in admixture.

The molarity of lithium salt as solute in the electrolyte is normally from 0.5 to 3 mols/l but is preferably from 0.5 to 2 mols/l. When the molarity of lithium salt falls below 0.5 mols/l or exceeds 2 mols/l, it is disadvantageous in that the electrolyte exhibits a low electrical conductivity that deteriorates the battery performance.

The material of the negative electrode constituting the battery of the invention is not specifically limited so far as it contains a carbon-based material capable of absorbing and releasing lithium. Specific examples of such a carbon-based material include pyrolysis product of organic material obtained under various pyrolysis conditions, artificial graphite, natural graphite, etc. Preferably, natural graphite produced by high temperature heat treatment of graphitizable pitch obtained from various materials, purified natural graphite or material obtained by subjecting these graphites may be mainly used. However, these graphite materials preferably have a d value (interlaminar distance) of from 0.335 to 0.34 nm, more preferably from 0.335 to 0.337 nm on lattice plate as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research. These graphite materials preferably have an ash content of not greater than 1% by weight, more preferably not greater than 0.5% by weight, most preferably not greater than 0.1% by weight, and a crystalline size (Lc) of not smaller

than 30 nm as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research.

Further, the crystalline size of the graphite is more preferably not smaller than 50 nm, most preferably not smaller than 100 nm. The median diameter of graphite material is from 1 to 100  $\mu\text{m}$ , preferably from 3 to 50  $\mu\text{m}$ , more preferably from 5 to 40  $\mu\text{m}$ , more preferably from 7 to 30  $\mu\text{m}$  as determined by laser diffractometry/scattering method. BET process specific surface area of graphite material is from 0.3 to 25.0  $\text{m}^2/\text{g}$ , preferably from 0.5 to 25.0  $\text{m}^2/\text{g}$ , more preferably from 0.7 to 20.0  $\text{m}^2/\text{g}$ , even more preferably from 0.7 to 15.0  $\text{m}^2/\text{g}$ , still even more preferably from 1.0 to 15.0  $\text{m}^2/\text{g}$ , still even more preferably from 1.5 to 10.0  $\text{m}^2/\text{g}$ . Moreover, the graphite preferably exhibits an intensity R ( $= I_B/I_A$ ) of from 0 to 0.5 wherein  $I_A$  is the peak intensity in the range of from 1,580 to 1,620  $\text{cm}^{-1}$  and  $I_B$  is the peak intensity in the range of from 1,350 to 1,370  $\text{cm}^{-1}$  as determined by Raman spectroscopy, and a peak half width of not greater than 26  $\text{cm}^{-1}$ , more preferably not greater than 25  $\text{cm}^{-1}$  in the range of from 1,580 to 1,620  $\text{cm}^{-1}$ .

Further, the carbon-based material may be used in admixture with a negative electrode material capable of absorbing and releasing lithium. Examples of the negative electrode material capable of absorbing and releasing lithium

other than carbon-based material include metal oxide material such as tin oxide and silicon oxide, metallic lithium, and various lithiumalloys. Two or more of these negative electrode materials may be used in admixture.

The process for the production of a negative electrode from these negative electrode materials is not specifically limited. The negative electrode can be produced, e.g., by optionally adding a binder, a thickening agent, an electrically-conducting material, a solvent, etc. to a negative electrode material to make a slurry, applying the slurry to a current collector substrate, and then drying the coated substrate. Alternatively, the negative electrode material may be rolled as it is to prepare a sheet-like electrode or may be compression-molded to prepare a pelletized electrode.

The binder to be used in the production of the electrode is not specifically limited so far as it is a material inert to the solvent to be used in the production of the electrode or the electrolyte. Specific examples of such a material include polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, isoprene rubber, butadiene rubber, etc.

Examples of the thickening agent include carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidized starch, phosphated starch, casein, etc.

Examples of the electrically-conducting material include metallic material such as copper and nickel, and carbon-based material such as graphite and carbon black.

As the material of the current collector for negative electrode there may be used a metal such as copper, nickel and stainless steel. Preferred among these metals is a copper foil because it can be easily formed into a thin film and from the standpoint of cost.

As the material of the positive electrode constituting the battery of the invention there may be used a material capable of absorbing and releasing lithium such as lithium transition metal composite oxide material, e.g., lithium cobalt oxide, lithium nickel oxide and lithium manganese oxide.

The process for the production of the positive electrode is not specifically limited. The negative electrode can be produced according to the foregoing process for the production of the negative electrode. Referring to the shape of the positive electrode, a binder, an electrically-conducting material, a solvent, etc. may be optionally added to and mixed with the positive electrode material which is then applied to a current collector substrate to form a sheet electrode or press-molded to form a pelletized electrode.

As the material of the current collector for positive electrode there may be used a metal such as aluminum, titanium and tantalum or alloy thereof. Particularly preferred among

these materials is aluminum or alloy thereof because it has a light weight and thus gives a high energy density.

The material and shape of the separator to be used in the battery of the invention are not specifically limited. However, the separator is preferably selected from materials which are inert to the electrolyte and have excellent liquid retaining properties. A porous sheet or nonwoven cloth made of a polyolefin such as polyethylene and polypropylene as a raw material is preferably used.

The process for the production of the battery of the invention having at least a negative electrode, a positive electrode and a non-aqueous electrolyte is not specifically limited but can be properly selected from those commonly employed.

The shape of the battery is not specifically limited. A cylinder type obtained by spirally winding a sheet-like electrode and a separator, a cylinder type having an inside out structure comprising a pelletized electrode and a separator in combination, a coin type having a pelletized electrode and a separator laminated on each other, etc. can be used.

The present invention will be further described in the following examples and comparative examples, but the present invention should not be construed as being limited thereto so far as they fall within the scope of the invention.

#### EXAMPLE 1

An electrolyte was prepared by dissolving a vinyl ethylene carbonate in a propylene carbonate in an amount of 5% by weight, and then dissolving thoroughly dried lithium hexafluorophosphate ( $\text{LiPF}_6$ ) as a solute in the solution in an amount of 1 mol/l in dried argon atmosphere.

To 94 parts by weight of KS-44 (trade name; produced by Timcal (??) Co., Ltd.), which is an artificial graphite powder having a d value of 0.336 nm on lattice plane (002 plane) as determined by X-ray diffractometry, a crystalline size ( $L_c$ ) of not lower than 100 nm (264 nm), an ash content of 0.04% by weight, a median diameter of 17  $\mu\text{m}$  as determined by laser diffractometry/scattering method, a BET process specific surface area of  $8.9 \text{ m}^2/\text{g}$ , an intensity R ( $= I_B/I_A$ ) of 0.15 wherein  $I_A$  is the peak intensity in the range of from 1,580 to 1,620  $\text{cm}^{-1}$  and  $I_B$  is the peak intensity in the range of from 1,350 to 1,370  $\text{cm}^{-1}$  as determined by Raman spectroscopy, and a peak half width of  $22.2 \text{ cm}^{-1}$  in the range of from 1,580 to 1,620  $\text{cm}^{-1}$  were added 6 parts by weight (solid content) of a dispersion of styrene-butadiene rubber (SBR) in distilled water. The mixture was then stirred by means of a disperser to make a slurry. The slurry thus made was uniformly applied to a copper foil having a thickness of 18  $\mu\text{m}$  as a negative electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare an electrode as a working electrode. A lithium foil was then provided as a counter electrode on the

working electrode with a separator impregnated with the electrolyte interposed therebetween to prepare a coin type half cell.

#### COMPARATIVE EXAMPLE 1

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving a vinylene carbonate in a propylene carbonate in an amount of 5% by weight, and then dissolving LiPF<sub>6</sub> in the solution in an amount of 1 mol/l was used.

#### COMPARATIVE EXAMPLE 2

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving LiPF<sub>6</sub> in a propylene carbonate in an amount of 1 mol/l was used.

#### EXAMPLE 2

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving a vinylethylene carbonate in a 1 : 1 (by volume) mixture of ethylene carbonate and diethyl carbonate in an amount of 2% by weight, and then dissolving LiPF<sub>6</sub> in the solution in an amount of 1 mol/l was used.

#### COMPARATIVE EXAMPLE 3

A coin type half cell was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving LiPF<sub>6</sub> in a 1 : 1 (by volume) mixture of ethylene carbonate and diethyl carbonate in an amount of 1 mol/l was used.

Subsequently, the coin type half cells of Examples 1 and 2 and Comparative Examples 1 to 3 thus prepared were subjected to cycle life test involving discharge with a constant current of 0.2 mA to a termination voltage of 0 V and charge with a constant current of 0.4 mA to a termination voltage of 1.5 V at 25°C.

The half cells of Examples 1 and 2 and Comparative Example 3 which had been subjected to 10 cycles of charge and discharge were stored in doped state at 60°C for 48 hours, subjected to dedoping, and then examined for storage properties.

The capacity-potential curve developed by charge and discharge at the 1st cycle in Example 1 and Comparative Examples 1 and 2 are shown in Figs. 1, 2 and 3, respectively. The term "capacity" as used herein is meant to indicate the capacity of the graphite used as a working electrode per weight.

The dedoped capacity (capacity of lithium dedoped from the working electrode) at the 1st cycle and the efficiency (dedoped capacity x 100/doped capacity) are set forth in Table 1.

As storage properties, the percentage of capacity of Examples 1 and 2 and Comparative Example 3 before (dedoped capacity at the 10th cycle) and after (dedoped capacity at the 11th cycle) storage are set forth in Table 2.

As shown in Fig. 3, in the case of single use of propylene carbonate as a solvent, a flat portion is observed in the vicinity

of 0.8 V where the decomposition of the electrolyte proceeds, disabling doping to 0 V. As shown in Fig. 2, when an electrolyte containing a vinylene carbonate is used, doping is made possible to 0 V, but the decomposition of the electrolyte cannot be sufficiently conducted. As shown in Fig. 1, the use of an electrolyte containing a vinylethylene carbonate makes it possible to inhibit the excessive decomposition of the electrolyte.

As can be seen in Tables 1 and 2, the use of an electrolyte containing a vinylethylene carbonate makes it possible to enhance efficiency while keeping a high capacity and improve storage properties at high temperature.

Table 1

	Dedoped capacity at 1st cycle (mAh/g)	Efficiency at 1st cycle (%)
Example 1	327	91.6
Example 2	314	91.6
Comparative Example 1	315	66.6
Comparative Example 2	-	-
Comparative Example 3	318	91.2

Table 2

	Storage properties (%)
Example 1	97.6
Example 2	97.1
Comparative Example 3	96.7

## EXAMPLE 3

To 85 parts by weight of LiCoO<sub>2</sub> as a positive active material were added 9 parts by weight of a polyvinylidene fluoride KF-1000 (trade name; produced by Kureha Chemical Industry Co., Ltd.). The mixture was then dispersed with N-methyl-2-pyrrolidone to

make a slurry. The slurry was uniformly applied to an aluminum foil having a thickness of 20  $\mu\text{m}$  as a positive electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a positive electrode.

To 95 parts by weight of KS-44 (trade name; produced by Timcal (??) Co., Ltd.), which is an artificial graphite powder having a d value of 0.336 nm on lattice plane (002 plane) as determined by X-ray diffractometry, a crystalline size (Lc) of not lower than 100 nm (264 nm), an ash content of 0.04% by weight, a median diameter of 17  $\mu\text{m}$  as determined by laser diffractometry/scattering method, a BET process specific surface area of  $8.9 \text{ m}^2/\text{g}$ , an intensity R ( $= I_B/I_A$ ) of 0.15 wherein  $I_A$  is the peak intensity in the range of from 1,580 to 1,620  $\text{cm}^{-1}$  and  $I_B$  is the peak intensity in the range of from 1,350 to 1,370  $\text{cm}^{-1}$  as determined by Raman spectroscopy, and a peak half width of  $22.2 \text{ cm}^{-1}$  in the range of from 1,580 to 1,620  $\text{cm}^{-1}$  as a negative active material were added 5 parts by weight of a polyvinylidene fluoride. The mixture was then dispersed with N-methyl-2-pyrrolidone to make a slurry. The slurry thus made was uniformly applied to a copper foil having a thickness of 18  $\mu\text{m}$  as a negative electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a negative electrode.

An electrolyte was prepared by dissolving a vinylethylene carbonate in a 1 : 1 (by volume) mixture of propylene carbonate

and ethylene carbonate in a proportion of 3% per 97% by weight, and then dissolving thoroughly dried lithium hexafluorophosphate ( $\text{LiPF}_6$ ) as a solute in the solution in an amount of 1 mol/l in dried argon atmosphere.

The positive electrode was then received in a stainless steel can which also acts as a positive electrode conductor. The negative electrode was then put on the positive electrode with a polyethylene separator impregnated with the electrolyte interposed therebetween. The can was then caulked with a sealing plate which also acts as a negative electrode conductor with an insulating gasket interposed therebetween to seal the can. Thus, a coin type battery was prepared.

#### COMPARATIVE EXAMPLE 4

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving  $\text{LiPF}_6$  in a 1 : 1 mixture (by volume) of propylene carbonate and ethylene carbonate in an amount of 1 mol/l was used.

#### EXAMPLE 4

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving a vinylethylene carbonate in a 1 : 1 mixture (by volume) of ethylene carbonate and  $\gamma$ -butyrolactone in a proportion of 3% per 97% by weight, and then dissolving  $\text{LiPF}_6$  in the solution in an amount of 1 mol/l was used.

#### COMPARATIVE EXAMPLE 5

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving LiPF<sub>6</sub> in a 1 : 1 mixture (by volume) of ethylene carbonate and  $\gamma$ -butyrolactone in an amount of 1 mol/l was used.

#### EXAMPLE 5

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving a vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and  $\gamma$ -butyrolactone in a proportion of 3% per 97% by weight, and then dissolving LiPF<sub>6</sub> in the solution in an amount of 1 mol/l was used.

#### COMPARATIVE EXAMPLE 6

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving LiPF<sub>6</sub> in a 1 : 1 mixture (by volume) of propylene carbonate and  $\gamma$ -butyrolactone in an amount of 1 mol/l was used.

#### EXAMPLE 6

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving a vinylethylene carbonate in propylene carbonate in a proportion of 3% per 97% by weight, and then dissolving LiPF<sub>6</sub> in the solution in an amount of 1 mol/l was used.

#### COMPARATIVE EXAMPLE 7

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving

LiPF<sub>6</sub> in propylene carbonate in an amount of 1 mol/l was used.

#### EXAMPLE 7

A coin type battery was prepared in the same manner as in Example 3 except that an electrolyte prepared by dissolving a vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and ethylene carbonate in a proportion of 5% per 95% by weight, and then dissolving LiPF<sub>6</sub> in the solution in an amount of 1 mol/l was used.

The batteries prepared in Examples 3 to 7 and Comparative Examples 4 to 7 were then subjected to cycle life test involving charge with a constant current of 0.5 mA to a termination voltage of 4.2 V and discharge to a termination voltage of 2.5 V at 25°C.

The electrical conductivity of the electrolytes used in Examples 3 to 7 at 20°C and -30°C are set forth in Table 3. For the measurement of electrical conductivity, an electrical conductivity meter (CM-30S, produced by DKK-TOA CORPORATION) was used.

The flash point was measured according to JIS K-2265.

The discharge capacity per weight of negative electrode and charge-discharge efficiency at the 1st cycle of the various batteries are set forth in Table 4. The charge-discharge efficiency was determined by the following equation.

Charge-discharge efficiency (%) = [(Discharge capacity)/(Charge capacity)] × 100

As shown in Table 4, Comparative Examples 4, 6 and 7 underwent violent decomposition of electrolyte and thus didn't act as battery.

On the other hand, the electrolytes of the examples of the invention didn't solidify even at - 30°C and exhibit a relatively high conductivity and thus provide an excellent capacity and charge-discharge efficiency when used in battery.

Table 3

	Electrical conductivity (mS/cm)		Flash point (°C)
	20°C	- 30°C	
Example 3	6.2	1.1	140
Example 4	9.1	2.6	119
Example 5	8.1	2.3	119
Example 6	5.3	1.0	138
Example 7	6.1	1.0	140

Table 4

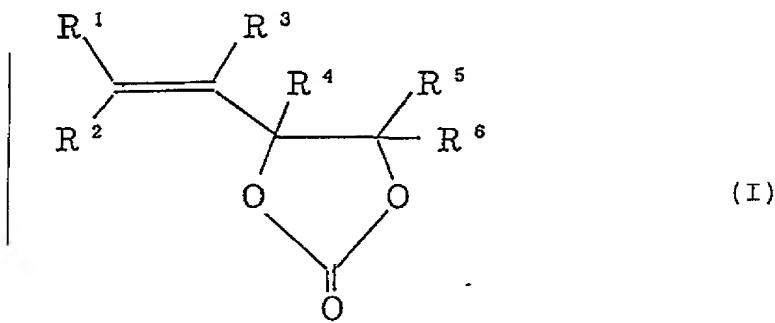
	Capacity at 1st cycle (mAh/g)	Efficiency at 1st cycle (%)
Example 3	226	81.3
Example 4	230	83.0
Example 5	213	81.1
Example 6	198	78.1
Example 7	233	84.4
Comparative Example 4	-	-
Comparative Example 5	120	34.4
Comparative Example 6	-	-
Comparative Example 7	-	-

### Industrial Applicability

In a non-aqueous electrolyte secondary battery comprising a negative electrode containing a carbon-based material, the use of a non-aqueous solvent containing a vinylethylene carbonate compound represented by the general formula (I) makes it possible to prepare a battery which is subject to minimized decomposition of the electrolyte and provides a high capacity as well as exhibits excellent storage properties and cycle life performance and hence contribute to the reduction of the size of and improve the performance of the non-aqueous electrolyte secondary battery.

## Claims

1. A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent, characterized in that said non-aqueous solvent contains a vinylethylene carbonate compound represented by the following general formula (I) in an amount of from 0.01% to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. The non-aqueous electrolyte secondary battery according to Claim 1, wherein said negative electrode contains a carbon-based material capable of absorbing and releasing lithium.

3. The non-aqueous electrolyte secondary battery according to Claim 2, wherein said carbon-based material capable of absorbing and releasing lithium comprises a carbon-based material having a d value of from 0.335 to 0.34 nm on lattice

plane (002 plane) as determined by X-ray diffractometry.

4. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 3, wherein said non-aqueous solvent is a mixed solvent containing a cyclic carbonate selected from the group consisting of alkylene carbonates the alkylene group moiety of which each have from 2 to 4 carbon atoms and a chain carbonate selected from the group consisting of dialkyl carbonate the alkyl group moiety of which each have from 1 to 4 carbon atoms except the vinylethylene carbonate compound of the general formula (I) each in an amount of not smaller than 20 vol-%, with the proviso that the content of said carbonates accounts for not smaller than 70 vol-% based on the total amount thereof.

5. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 3, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the general formula (I) contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 and exhibits a flash point of not lower than 70°C.

6. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 3, wherein said non-aqueous solvent except the vinylethylene carbonate compound of the general formula (I) is selected from solvents having a relative dielectric constant of not smaller than 25.

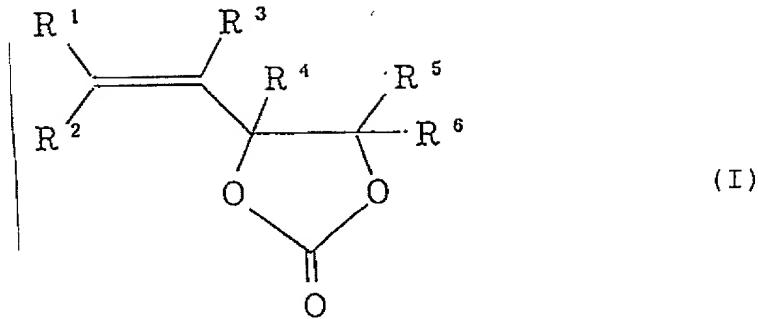
7. The non-aqueous electrolyte secondary battery

according to Claim 5 or 6, wherein said solvent having a relative dielectric constant of not smaller than 25 is selected from ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone.

8. The non-aqueous electrolyte secondary battery according to Claim 5 or 6, wherein said solvent having a relative dielectric constant of not smaller than 25 is a mixture of ethylene carbonate and  $\gamma$ -butyrolactone.

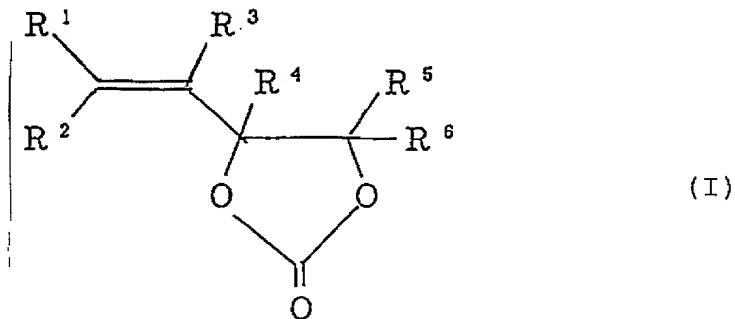
9. The non-aqueous electrolyte secondary battery according to any one of Claims 1 to 8, wherein said lithium salt is at least one salt selected from LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>.

10. A non-aqueous electrolyte for non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium which comprises a solute and a non-aqueous solvent, characterized in that said non-aqueous solvent contains a vinylethylene carbonate compound represented by the following general formula (I) in an amount of from 0.01 to 20% by weight:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

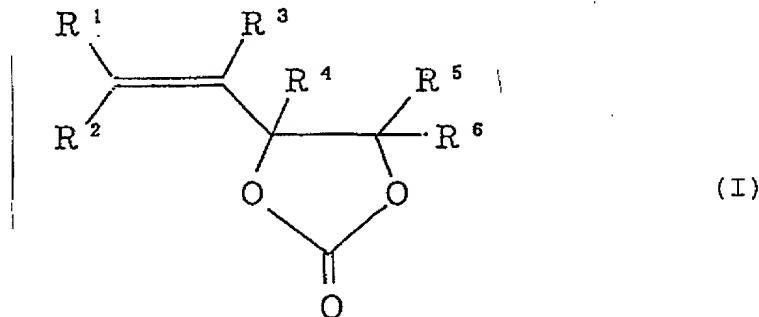
11. A non-aqueous electrolyte for non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium which comprises a solute and a non-aqueous solvent, characterized in that said non-aqueous solvent contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the following general formula (I) incorporated therein:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

### Abstract

A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode and an electrolyte having a lithium salt dissolved in a non-aqueous solvent characterized in that said non-aqueous solvent contains a vinylethylene carbonate compound represented by the general formula (I) in an amount of from 0.01 to 20% by weight is subject to minimized decomposition of the electrolyte and can provide a high capacity as well as exhibits excellent storage properties and cycle life performance.

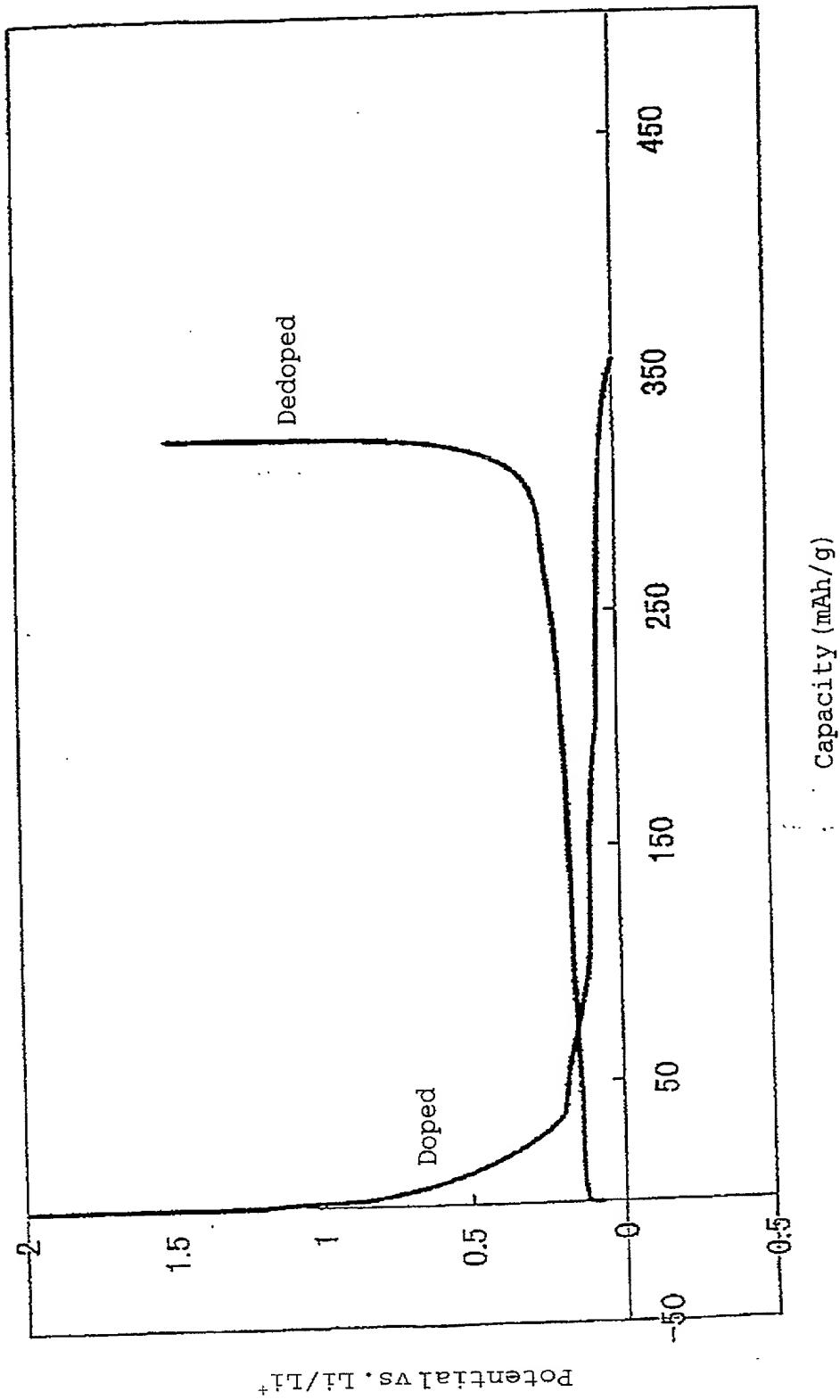


wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

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FIG. 1

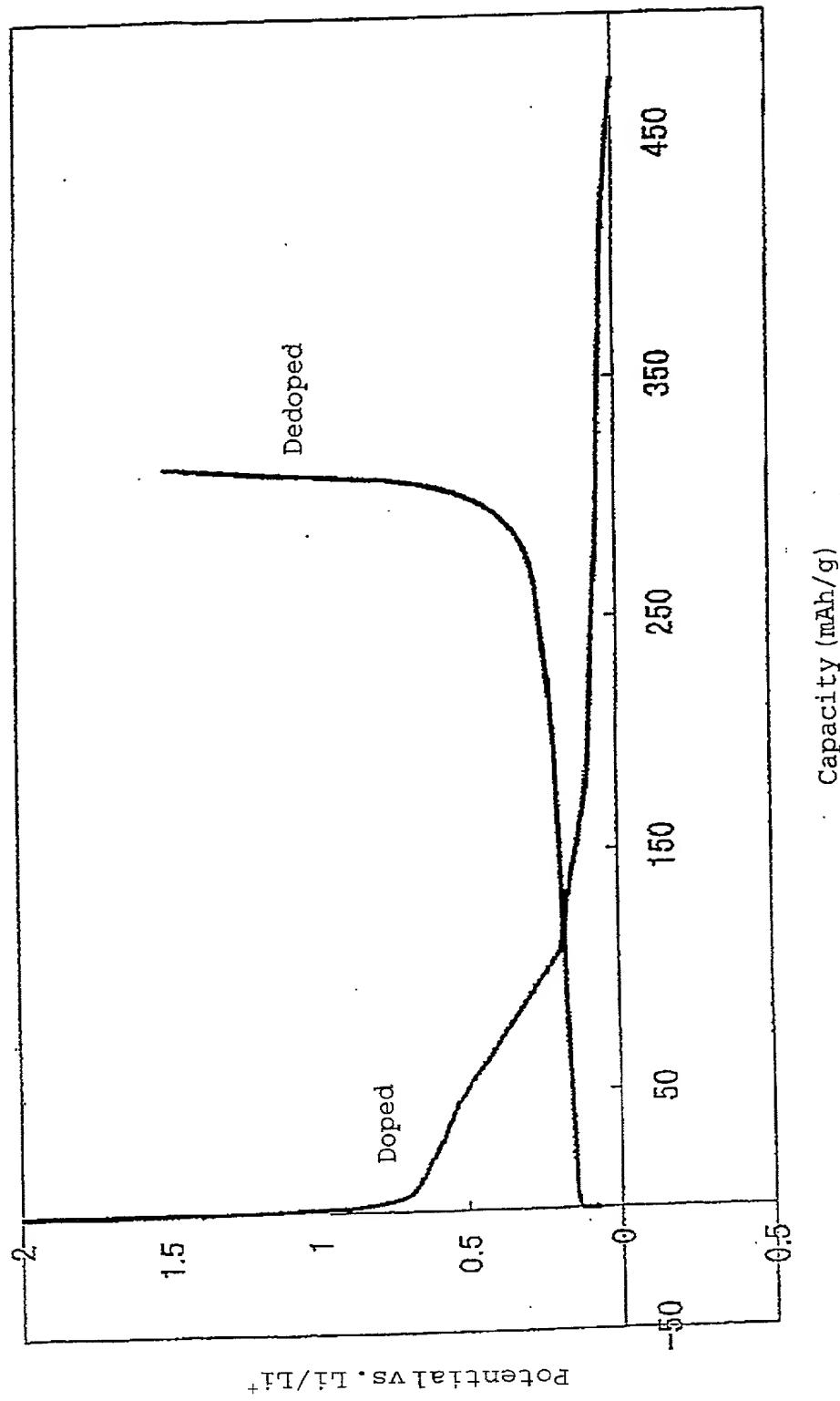


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FIG. 2

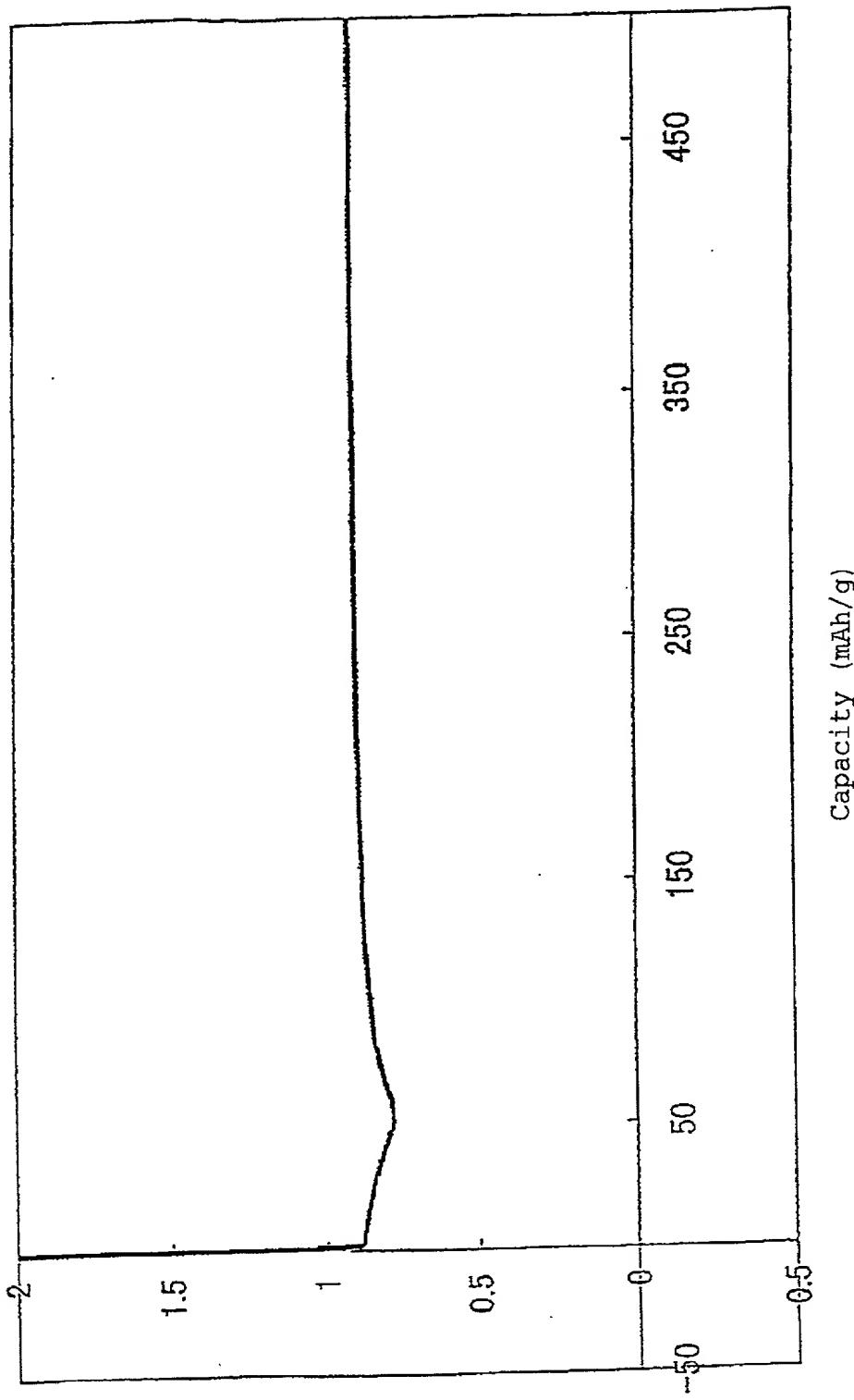


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FIG. 3

Potential vs.  $\text{Li}/\text{Li}^+$

## Declaration and Power of Attorney For Patent Application

### 特許出願宣言書及び委任状

## Japanese Language Declaration

## 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

**As a below named inventor, I hereby declare that:**

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

# NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

上記発明の明細書は、

the specification of which

- 本書に添付されています。

\_\_\_\_月\_\_\_\_日に提出され、米国出願番号または特許協定条約国際出願番号を\_\_\_\_\_とし、  
(該当する場合) \_\_\_\_\_に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

**Japanese Language Declaration**  
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一ヵ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)

外国での先行出願

P.Hei. 11-172405  
(Number)  
(番号)  
P.Hei. 11-304847  
(Number)  
(番号)

Japan  
(Country)  
(国名)  
Japan  
(Country)  
(国名)

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed	
優先権主張	
<input checked="" type="checkbox"/>	<input type="checkbox"/>
Yes はい	No いいえ
<input checked="" type="checkbox"/>	<input type="checkbox"/>
Yes はい	No いいえ

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

PCT/JP00/03910  
(Application No.)  
(出願番号)

15/June/2000  
(Filing Date)  
(出願日)

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

Pending

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰され、そしてそのような故意による虚偽の声明を行なえば、又は既に許可された特許の有効性が失われることを、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration  
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。  
(弁護士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



022850

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Send Correspondence to:



022850

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発明者の署名	日付	Inventor's signature <u>Minoru Kotato</u>	Date May 20, 2002
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国籍	Citizenship Japan		
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第二の共同発明者の署名	日付	Second joint Inventor's signature <u>Takashi Fujii</u>	Date May 20, 2002
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(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)

## Japanese Language Declaration

(日本語宣言書)

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第三の共同発明者の署名	Third joint Inventor's signature <i>Noriko Shima</i>
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第四の共同発明者の氏名	4- Full name of fourth joint inventor, if any Hitoshi SUZUKI
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第五の共同発明者の氏名	Full name of fifth joint inventor, if any
第五の共同発明者の署名	Fifth joint Inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

第六の共同発明者の氏名	Full name of sixth joint inventor, if any
第六の共同発明者の署名	Sixth joint Inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)